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To : Mike Kosakowski, Headquarters, U.S. EPA ✓ Date: February 8, 1982
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PAH Analytical Methods (High Performance Liquid Chromatography)

There has been some discussion during the past month regarding the differences between MDH methods for PAH analyses and the Method 610. It is true that there are significant differences between the two high performance liquid chromatography (HPLC) methods, as noted in the Koppers Coke letter of January 8, 1982, to Terry Kasen. These differences include sample clean-up procedures, extraction solvents, field sample size, injection sample size, type of equipment, and number of detectors. The MDH does feel that the methods employed are optimum procedures for the types of samples normally handled. The differences between the two methods are as follows:

1) Sample Cleaning: Method 610 utilizes a sample clean-up procedure prior to injection. This clean-up is primarily designed to separate the different organic fractions from the extract prior to injection. This strategy is useful in analyzing heavily contaminated samples. The MDH method involves no such clean-up since most samples are collected from municipal wells that typically have very dilute concentrations of contaminants. With such low concentrations, clean-up is not necessary and may actually be detrimental to maximizing PAH recovery in the extract. Currently, MDH simply dilutes those samples that are heavily contaminated, which may result in rather high detection limits.

2) Extraction Solvents: Method 610 utilizes methylene chloride while MDH uses cyclohexane. Cyclohexane is a good solvent for extracting PAH's with minimal extraction of other fractions while methylene chloride is a broad purpose solvent. The Department is simply attempting to be more selective.

3) Original Sample Size: Method 610 involves an extraction from 1-liter field samples with the sample being reduced to an extract of 10-ml or less. The Department utilizes a 4-liter field sample, which is reduced to a 4-ml extract. The Department is attempting to maximize field sample size and minimize extract size, which yields the highest PAH concentrations in the extract and more sensitive analytical results.

4) Injection Sample Size: Method 610 involves an injection of 5-20 microliters of extract while MDH uses 200 microliters of extract. Again, MDH is attempting to maximize the amount of PAH molecules available for detection.

5) Type of Equipment: Method 610 utilizes reverse-phase liquid chromatography which has the advantages of more precise absolute retention times and column rejuvenation. The Department uses normal-phase liquid chromatography, which depends upon relative retention times. Currently, MDH does not have the equipment for reverse-phase liquid chromatography.

6) Number of Detectors: Method 610 uses a fluorescent detector, which may or may not be coupled with an ultraviolet detector. Some labs use only the fluorescent detector. The Department uses a fluorescent detector and two ultraviolet detectors (254nm and 280nm) and usually conducts two injections (fluorescent - U.V. - 254nm, fluorescent - U.V. 280nm).

On any given sample, there are two injections. Thus, there is always confirmation of a given run. The use of 3 detectors is much more discriminating in identifying particular compounds and enables one to determine the level of confidence in assessing whether or not the compound identified by one detector is actually that compound.

In summary, there are significant differences between Method 610 and the MDH method. However, the MDH method is particularly sensitive to reliably detecting low concentrations of PAH's in relatively dilute samples.

MPC:lss

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